UNIVERSITI PUTRA MALAYSIA

EVALUATION OF POLYMERIC ADSORBENTS FOR THE REFINING OF CRUDE PALM OIL

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By

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LIST OF ABBREVIATIONS

CPO	Crude Palm Oil
IPA	Isopropanol
FFA	Free Fatty Acid
BHA	Butylhydroxy Anisole
PFAD	Palm Fatty Acid Distillates
RBD	Refined Bleached Deodorised
BJH	Barrett-Joyner-Halenda

NOMENCLATURE

		Units in S.I System
A	Column's cross sectional area	(m^2)
B	Permeability	(m^2)
D	Column's diameter	(m)
D	Diffusion Coefficient	(m^2/s)
d_p	Particle diameter	(m)
ε	Voidage	
f_w	Correction factor	
k	Mass Transfer Coefficient	(m/s)
l	Length of column	(m)
S	Specific Surface Area	(m^2/m^3)
S_B	Specific surface area of the bed	(m^2/m^3)
u	Superficial velocity	(m/s)
μ	Dynamic viscosity	(kg/ms)
ν	Kinematic viscosity	(m^2/s)
ρ	Density	(kg/m^3)

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Faculty: Engineering

Three types of adsorbents namely EXA 31, EXA 32 and EXA 50 were tested for their ability to refine CPO. These polymers are made up of styrene DVB copolymer without functional group and ionic form. The adsorption process was carried in packed column with temperature maintained at 50°C flowrate of 2 ml/s and 70°C for flowrate of 0.1 ml/s. EXA 50 recorded the highest adsorption capacity of 0.31 mg of carotene per gram of adsorbent at this flowrate. EXA 32 and EXA 31 recorded adsorption capacity of 0.29 mg and 0.18 mg carotene per gram of adsorbent.

The regeneration efficiency for EXA 31 tends to decrease with the increase in the number of runs. After five runs the regeneration efficiency was at 47.8%. The regeneration efficiency of EXA 32 initially increases but was followed by a decrease. After five runs the regeneration efficiency was at 78.2%. The regeneration efficiency of EXA 50 increases with the increase in the number of runs. This is an important finding as it indicates that the adsorbent could be used for a longer period of time without much deterioration to its adsorption capacity.

Performance study for the low flow (0.1 ml/s) was carried out only on the best adsorbent EXA 50. The effect of flowrate on carotene adsorption capacity and regeneration efficiency could be determine by comparing the results for the high flow (2 ml/s) and the low flow (0.1 ml/s). Carotene concentration in the hexane fraction for the 0.1 ml/s flow (17500ppm) was 17 times higher than that in the high flow (986 ppm). The amount of carotene adsorbed per gram of adsorbent also increased by 25% from 0.31 mg/g to 0.39 mg/g. The regeneration efficiency also recorded improvement that was from 66.2% for the high flow to 79% for the low flow.

The adsorption isotherms were determined by using different concentrations of carotene in IPA and hexane. At low concentrations all three adsorbents showed linear isotherms in IPA and Langmuir isotherms in hexane. The results obtained from batch test matches with those from packed column.

All three types of adsorbents also exhibit ability to adsorbed FFA. The results showed reduction of percentage of FFA in the oil, IPA, and hexane fraction in both EXA 32 and EXA 50. Removal of FFA was also recorded oil and hexane fraction in EXA 31.but there was an increase in the IPA fraction. This means that IPA has the ability to elute FFA. EXA 31, EXA 32, and EXA 50 recorded an average reduction of the percentage of FFA in the oil fraction to 2.4%, 0.93% and 1.8% respectively as compared to the crude with 3.44% FFA.

All three types of adsorbent also showed the ability to remove phosphorus which exist in the form of phospholipids in CPO. The removal of phosphorus was observed in all the three fraction (oil, IPA, and hexane). The concentration of phosphorus in the CPO was 21.42. The percentage of phosphorus removal ranges from 31.6% to 45.5% in the oil fraction, 7.6% to 29% in the IPA fraction, and 14.7% to 16.4% in the hexane fraction in EXA 31. Percentage of phosphorus removal ranges from 14.1% to 34.1% in the oil fraction, 15.4% to 35.8% in the IPA fraction, and 26% to 66.1% in the hexane fraction in EXA 32. EXA 50 recorded percentage of phosphorus removal ranging from 5.3% to 44.2% in the oil fraction, 36.9% to 80.9% in the IPA fraction, and 15.3% to 77.9% in the hexane fraction.

All three types of adsorbent showed the ability to remove colour. Results also showed that the redness of the oil is proportional to the carotene concentration. The higher the redder the colour of the oil the higher the carotene concentration.

An increase in the PV was observed in all the three fractions. This indicates that oxidation has occurred to the oil. The reason behind this oxidation could mainly be due to the removal of the oil natural antioxidant (carotene, tocopherols and tocotrienols) and long storage prior analysis. This problem could be overcome by adding an antioxidant like BHA (Butylhydroxy anisole) into the oil before the study was carried out. Oil fraction from EXA 31, EXA 32, and EXA 50 recorded an increase from 52.8% to 372% of PV. IPA fraction from EXA 31, EXA 32, and EXA 50 recorded an increase from 2.8 to 336% of

PV. Hexane fraction from EXA 31, EXA 32, and EXA 50 recorded an increase of 16.7% to 639% of PV.

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Oleh

STEPHEN YOONG

Mei 1999

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Fakulti: **Kejuruteraan**

Tiga jenis penjerap EXA 31, EXA 32 dan EXA 50 diuji kebolehannya untuk menulenkan minyak sawit mentah. Penjerap-penjerap ini diperbuat daripada ko-polimer styrene DVB tanpa kumpulan berfungsi dan bentuk ionik. Proses penjerapan dilakukan dalam tiub berisi bahan penjerap dan suhu ditetapkan pada 50°C dan kadar alir 2 ml/s dan pada 70°C dan kadar alir 0.1 ml/s. EXA 50 mencatatkan keupayaan penjerapan yang paling tinggi iaitu 0.31 mg karotin bagi setiap gram bahan penjerap. EXA 32 dan EXA 31 pula mencatatkan keupayaan penjerapan 0.29 mg dan 0.18 mg karotin bagi setiap gram bahan penjerap.

Kecekapan jana-semula EXA 31 berkurang dengan bertambahnya kali kitar kajian. Selepas lima kitar, kecekapan jana-semula ialah 47.8%. Kecekapan jana-semula EXA 32 bertambah pada awalnya diikuti dengan pengurangan. Selepas lima kitar, kecekapan jana-semula adalah pada 78.2%. Kecekapan jana-semula EXA 50 bertambah dengan bertambahnya bilangan

kitar. Ini adalah suatu penemuan yang penting kerana ini menandakan bahawa bahan penjerap ini boleh digunakan untuk jangka yang lebih lama tanpa kemerosotan yang banyak atas keupayaan jerapnya.

Kajian ke atas persembahan pada kadar alir rendah 0.1 ml/s dijalankan pada bahan penjerap yang terbaik sahaja iaitu EXA 50. Kesan kadar alir ke atas keupayaan penjerapan karotin dan keupayaan jana-semula dapat ditentukan dengan perbandingan keputusan untuk kadar alir tinggi (2 ml/s) dan kadar alir rendah (0.1 ml/s). Kepekatan karotin dalam pecahan hexan untuk kadar alir 0.1 ml/s (17500 bpj) adalah 17 kali lebih tinggi daripada yang dalam kadar alir 2 ml/s (956 bjp). Amaun karotin yang dijerap juga bertambah sebanyak 25% iaitu dari 0.31 mg/g kepada 0.39 mg/g. Keupayaan jana-semula juga mencatatkan peningkatan dari 66.2% untuk kadar alir tinggi kepada 79% untuk kadar alir rendah.

Isoterma-isoterma penjerapan ditentukan dengan menggunakan kepekatan karotin yang berlainan di dalam IPA dan hexane. Pada kepekatan karotin yang rendah ketiga-tiga bahan penjerap menunjukkkan isoterma linear di dalam IPA dan isoterma Langmuir di dalam hexan. Keputusan yang diperolehi melalui ujian secara sesekumpul juga hampir sama dengan yang diperolehi melalui tiub berisi bahan penjerap (packed column).

Ketiga-tiga bahan penjerap juga menunjukkan keupayaan untuk menjerap molekul-molekul asid lemak bebas. Keputusan menunjukkan pengurangan dalam peratus asid lemak bebas dalam pecahan minyak, IPA, dan lemak bebas juga diperhatikan dalam pecahan minyak dan hexane bagi EXA 31 tetapi pertambahan dicatatkan dalam pecahan IPA. Ini menunjukkan bahawa IPA berkebolehan untuk mengelusi (elute) asid lemak bebas. EXA 31, EXA 32, dan EXA 50 mencatatkan purata pengurangan peratus asid lemak bebas dalam pecahan minyak kepada 2.4%, 0.93%, dan 1.8% masing-masing berbanding dengan minyak mentah 3.44%.

Ketiga-tiga bahan penjerap juga menunjukkan keupayaan untuk mengurangkan kandungan fosforus minyak yang wujud dalam bentuk fosfolipid. Pengurangan fosforus dapat diperhatikan dalam pecahan minyak, IPA, dan hexane. Kepekatan fosforus bagi minyak sawit mentah 21.42. Peratus penyingkiran fosforus adalah dalam julat 31.6% ke 45.5% dalam pecahan minyak, 7.6% ke 29% dalam pecahan IPA, dan 14.7% ke 16.4% dalam pecahan hexane dalam EXA 31. Peratus penyingkiran fosforus adalah dalam julat 14.1% ke 34.1% dalam pecahan minyak, 15.4% ke 35.8% dalam pecahan IPA, dan 26% ke 66.1% dalam pecahan hexane dalam EXA 32. EXA 50 mencatatkan peratus penyingkiran fosforus dalam julat 5.3% ke 44.2% dalam pecahan minyak, 36.9% ke 80.9% dalam pecahan IPA, dan 15.3% ke 77.9% dalam pecahan minyak.

Ketiga-tiga bahan penjerap juga menunjukkan keupayyan untuk mengurangkan warna minyak. Keputusan dari penyingkiran minyak menunjukkan kemerahan warna minyak adalah berkadaran dengan kepekatan karotin. Semakin tinggi kepekatan karotin semakin merah warna minyak itu.

hexane di dalam kedua-dua EXA 32 dan EXA 50. Pengurangan peratus asid lemak bebas juga diperhatikan dalam pecahan minyak dan hexane bagi EXA 31 tetapi pertambahan dicatatkan dalam pecahan IPA. Ini menunjukkan bahawa IPA berkebolehan untuk mengelusi (elute) asid lemak bebas. EXA 31, EXA 32, dan EXA 50 mencatatkan purata pengurangan peratus asid lemak bebas dalam pecahan minyak kepada 2.4%, 0.93%, dan 1.8% masing-masing berbanding dengan minyak mentah 3.44%.

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Peningkatan nilai PV dicatatkan dalam ketiga-tiga pecahan minyak. Ini menunjukkan pengoksidaan telah berlaku kepada minyak itu. Pengoksidaan minyak berlaku kerana anti-oksida semulajadi minyak (karotin, tokoferol, dan tokotrienol) telah disingkirkan dan penyimpanan minyak dalam jangkamasa yang agak lama sebelum analisa. Masalah ini dapat diatasi dengan penambahn anti-oksida seperti BHA (Butylhydroxy anisole) kepada minyak sebelum kajian dilakukan. Pecahan minyak bagi EXA 31, EXA 32, dan EXA 50 mencatatkan peningkatan PV dalam julat 52.8% ke 372%. Pecahan IPA bagi EXA 31, EXA 32, dan EXA 50 mencatatkan peningkatan PV dalam julat 2.8% ke 336%. Pecahan hexane pula mencatatkan peningkatan PV dalam julat 16.7% ke 639%.

CHAPTER I

INTRODUCTION

Malaysia is one of the leading producers and exporters of palm oil, accounting for over 50% of the world output and almost 75% of world export. The Malaysian Crude Palm Oil (CPO) production for 1990 was 6.092 million tonnes making it Malaysia's number one export commodity. It is estimated that by year 1999 Malaysia will produce 9.06 million tonnes of palm oil. Based on the current CPO oil price of RM1300 per tonne this is equivalent to RM 11.8 billion (PORIM).

Malaysia's achievement in the development of the palm oil industry within a short period of time has received international recognition. It is one of the most impressive success stories in agriculture. It is entirely through fair competition, active promotion and quality research and development that Malaysia has been able to develop the palm oil industry. Today, Malaysia is proud to see that palm oil is the world's largest traded vegetable oil. In order to continue the commanding lead in the oil industry better processing and refining methods needs to be developed. The technology and techniques should be developed in such a manner that the industry is competitive even under most unfavourable market conditions. Thus, in this study we examine the possibilities of separating vitamin E, carotenes, phospholipids and free fatty acids from CPO. Vitamin E and carotenes which is a precursor of vitamin A, have high economic values due to its medicinal properties (PORIM).

Choo *et al.* (1996) reported that CPO contains small amounts of free fatty acids (FFA), phosphatides, moisture, flavour components, and other trace compounds, including the nutritionally important carotenoids (500-700ppm) and vitamin E (600-1000 ppm). Except for some vitamin E, these components, including the carotenoids, are removed from the oil during the refining process. As a result, various methods of extraction and recovery have been developed and employed to recover these valuable constituents from palm oil. These include extraction by saponification (Eckey, 1945, 1949; Tabor *et al.*, 1948; Gebhert, 1951; Blaizot, 1953), adsorption (Ong and Boey, 1980, Lange and Flozenogen, 1949; Mamuro *et al.*, 1986; Hama *et al.*, 1987; Badlishah *et al.*, 1998), precipitation (Knafo, 1952), selective solvent extraction (Passino, 1952; Larner, 1947), molecular distillation (Ooi *et al.*, 1986), transesterification followed by distillation (Lion Fat and company, 1976; Hama *et al.*, 1986, 1988) and others (Choo *et al.*, 1987). However, only transesterification and distillation have been further developed into commercial-scale processes (Iwasaki and Murakoshi, 1992). This unique process has already been put into industrial production by Lion Corporation of Japan in Sakaide. In this process, however no edible triglyceride is obtained due to the chemical conversion of these triglycerides to methyl esters.

The preservation of valuable products such as vitamin E and β-carotene can be accomplished by adopting a milder process like adsorption. Another advantage of the adsorption process is that the bleaching process that acts to remove impurities could be avoided. The bleaching process produces a high amount of bleaching earth that poses great environmental problem in disposal. An added advantage is that the adsorbent can be regenerated and re-use over and over again. This will also save the refiners substantial amount of money as for every 1000 tonnes of oil processed 1 tonne of oil is lost in the cake of the bleaching earth. Based on the current CPO price, this can save refiner RM 1300 (based on the 1999 price) for every 1000 tonnes of oil processed. This will save the palm oil industry RM 11.8 million based on 1999 CPO production. Besides that, carotenes and vitamin E recovered from this process can also be sold.

The objectives of this study are:

a) to determine the efficiency of the adsorbent in adsorbing β carotene, vitamin E, free fatty acids and phospholipids

b) to study the regeneration capability of the adsorbent

c) determine the adsorption isotherm of the process

CHAPTER II

LITERATURE REVIEW

Physical Adsorption

Sorption is the selective transfer of one or more solutes from a fluid phase to a batch of rigid particles. The usual selectivity of an adsorbent between solute and carrier fluid or between different solutes makes it possible to separate certain solutes from the carrier or from one another. Similarly, a reverse operation, desorption, will often bring about separation of species from the solid.

Adsorption involves, in general, the accumulation of solute molecules at an interface. The accumulation per unit area is small, thus, highly porous solids with very large internal area per unit volume are preferred. At ordinary temperatures, intermolecular forces usually cause adsorption (primarily from Van der Waals forces) rather than by formation of new chemical bonds; this is then called physical adsorption, or physisorption. Figure 1 shows the means of uptake and storage of solutes by an adsorbent particle in its pores and on its pores surfaces. Whether the adsorbent is handled as fixed bed or fluidised bed,